Cateto, C.A., Naceur, M.N., Rodrigues, A.E., Barreiro, M.F., **"Lignin characterization by acetylation procedures"**, 9th International Chemical Engineering Conference – CHEMPOR 2005, Coimbra, Portugal, 21-23 September (2005) (*poster*)

CHEMPOR 2005

Coimbra – 21st – 23rd September 2005

PROGRAMME

Wednesday 21 st September

18:00-19:30 Welcoming participants

Thursday 22nd September

Anfiteatro 1

08:30-09:00 Welcoming participants

09:00-09:30 Opening Session

Session 1 Chairpersons: *F. Ramôa Ribeiro* and *Lélio Quaresma Lobo*

09:30-10:15 Invited Lecture: Dr.Trevor Evans (Chief Executive& Secretary IchemE);
"The role of National Societies and the European Federation of Chemical Engineering in promoting a better appreciation of chemical engineering as an essential contributor to the quality of life and to achieving a suitable future."

10:15-11:00 Invited Lecture: Prof. Jens Nielsen (Technical University of Denmark)
"The role of chemical engineering in modern biotechnology."

11:00-11:15 Coffee Break

Anfiteatro 1

Session 2 Chairpersons: *Moura Bordado* and *Salvador Pinheiro*

11:20-12:05 Invited Lecture Engº C. Pedro Nunes (CUF)
Uma Perspectiva Estratégica da Indústria da Refinação de Petróleos e Petroquímica em Portugal.
Chairpersons: *Moura Bordado* and *Salvador Pinheiro*

12:05-12:25 IP006- **Methylacetylene and Propadiene Reactors Optimization in the Sines Repsol Steam Cracker Plant**
André A.Vilelas, José P. Braga
Interface Team, Olefins Plant, Repsol Steam Cracker,Sines, Portugal.

12:25-12:45 IP034- **Study and optimization of a hydrogen distribution network: refinery case study**
André Fonseca, Vítor Sá, Hugo Bento, Manuel L.C. Tavares, Luísa A.C.N. Gomes
Chemical Engineering Department, Instituto Superior de Engenharia, IPP, Porto;
Technology Area, Galp Energia, 4451-852 Leça da Palmeira, Portugal.

12:45-13:05 IP010- **Separation of branched hexane isomers on zeolite BETA**
Patrick S. Bárcia, José A. C. Silva, Alírio E. Rodrigues
Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança;
Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, FEUPorto.

13:05-13:25 IP068- **Recuperação do ciclohexanol e da ciclohexanona do processo de produção de anilina**
Fernando P. Mendes, Marco A. F. Prior, Rui M. F. Andrade, Susana C. G. Caldas, Mário Jorge O. Pinho, Laura M. T. Santos, Luís M. Castro, Nazaré C. Pinheiro, Manuel A. Ramos, Belmiro P. M. Duarte
Quimigal S.A., Química de Portugal, Portugal;
Departamento de Engenharia Química, Instituto Superior de Engenharia de Coimbra.

13:25-13:45 MSC031-**Multivariate analysis of the benzene nitration process for pollution prevention**
Paulo A. Quadros, Marco S. Reis, Cristina M. S. G. Baptista
Gepsi-PSE Group, Chemical Engineering Department, University of Coimbra.

Anfiteatro 2

Session 3 Chairpersons: *Alírio Rodrigues* and *Rosa Quinta Ferreira*

12:05-12:25 ESF005-**Efeito protector da matriz em catalisadores de "cracking" catalítico em relação ao envenenamento por bases azotadas**
G. Caeiro, Patrick Magnoux, J.M. Lopes e F. Ramôa Ribeiro
CEBQ, Instituto Superior Técnico, Lisboa ; Lab. de Catalyse en Chimie Organique, Poitiers, France

12:25-12:45 ESF021- **Degradação fotocatalítica de corantes têxteis**
Edilberto T. Soares, Marla A. Lansarin, Celso C. Moro, Cristina L. Souza e Natália Klafke

16:25-16:45 ESF051- **Effect of hydrodynamic conditions in osmotic evaporation using membrane contactors**
V. D. Alves, I. M. Coelhoso
REQUIMTE / CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa.

Anfiteatro 3

Session 16 Chairpersons: *Ana Paula Póvoa and Adélio Mendes*

16:05-16:25 QL082-**Protein recovery from tannery wastewater containing chromium by nitrogen removal**
Francisco N.S. Basilio, Helder F.C. Marques, Marta I.G. Sousa, Raquel A.P. Silva, Nídia S. Caetano
Chemical Engineering Department, Instituto Superior de Engenharia do Porto;
LEPAE, Chemical Engineering Department, Instituto Superior de Engenharia do Porto.

16:25-16:45 QL111-**Preparation of Therapeutic Contact Lenses Using Supercritical and Compressed Fluids**
Hermínio C. de Sousa, Ana Rita C. Duarte, Joana P. Guerra, Viviana P. Costa, Eugénio O.B. Leite, Catarina M.M. Duarte, Maria H. Gil
Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra;
Instituto de Biologia Experimental e Tecnológica, Oeiras;
Faculdade de Ciências da Saúde, Universidade da Beira Interior, Covilhã.

Anfiteatro 4

Session 17 Chairpersons: *António Portugal*

16:05-16:25 QL115-**Life Cycle Assessment of bioethanol from sugar beet and wheat – comparison with gasoline**
João Malça, Fausto Freire
Mechanical Engineering Department, ISEC, Coimbra Polytechnic Institute;
Mechanical Engineering Department, Faculty of Sciences and Technology, University of Coimbra.

16:25-16:45 QL090-**The emergence of a new field of application of chemical and systems engineering principles: pharmaceutical engineering**
José Cardoso de Menezes
Centre for Chemical & Biological Engineering, IST, Technical University of Lisbon.

16:45-17:00 Coffee Break

Anfiteatro 1

Session 18 Chairpersons: *Sebastião Feyo de Azevedo* and *Pedro Saraiva*

17:00-17:40 Chemical Engineering Education – Prof. Robert Armstrong, MIT, USA
"Frontiers in Chemical Engineering Education."

17:40-18:40 Forum Chemical Engineering Education

18:40-19:00 Closing Session

POSTER SESSIONS

Thursday 22nd September

17:20-19:00 Chemical Engineering Department

ESF-Engineering Sciences and Fundamentals

ESF001 - **Mass transfer to clean bubbles at low turbulent energy dissipation**
Sebastião S. Alves, Jorge M. T. Vasconcelos, Sandra P. Orvalho,
Centro de Eng. Biológica e Química, Dept. of Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal.

ESF003 - **Plug Formation and Flow Regimes in Dense-Phase Pneumatic Conveying**
Fernando A. V. Silvano, Severino S. Pandiella
Departamento de Engenharia Mecânica, Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Leiria, Leiria, Portugal.
School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester, U. K.

ESF004 -**Dynamic model of a supercritical carbon dioxide heat exchanger**
João B. Fernandes, Pedro C. Simões, José Paulo Mota
REQUIMTE, Chemistry Department, University Nova of Lisbon, Quinta da Torre, Caparica, Portugal.

ESF006 -**Safety study for scaleup of dehydroabietic acid**
Carlos Lopes, Carla Raminhos, João A.A. Lourenço
Instituto Nacional de Engenharia e Tecnologia Industrial, Lisboa, Portugal.

LEPAE – Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Porto, Portugal.

IP016 -**Novos materiais de eléctrodo do tipo espinela para a degradação electroquímica do clorofórmio**
Sandra Ferreira, M. Helena Mendonça, M. Rosa Nunes, M. I. da Silva Pereira, Fernanda Costa, J. M. Nogueira
Departamento de Química e Bioquímica, Centro de Ciências Moleculares e Materiais, Faculdade de Ciências, Universidade de Lisboa, Lisboa, Portugal.

IP018 -**Estudo comparativo da extração do ácido clavulânico por solvente orgânico e sistemas de duas fases aquosas**
Luciana Machado Brites, Daniela Bataglia Hirata, Marlei Barboza Pasotto, Carlos Osamu Hokka
Departamento de Engenharia Química, Universidade Federal de São Carlos, São Carlos, SP, Brasil.

IP019 -**Validação de modelo teórico para a purificação de ácido clavulânico em resina polimérica de troca iônica.**
Marina T.A.G.Mendes, Marlei Barboza Pasotto, Wu Hong Kwong, Carlos Osamu Hokka
Departamento de Engenharia Química, Universidade Federal de São Carlos, São Carlos, SP, Brasil.

IP021 -**Impact of lignin quality (h/g ratio) in kraft pulping of Maritime pine**
Ana Alves, Helena Pereira, Denilson da Silva Peres, Guillaume Chantre and José Rodrigues
Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade Técnica de Lisboa, Lisboa, Portugal;
Instituto de Investigação Científica Tropical, Centro de Estudos de Tecnologia Florestal, Lisboa, Portugal;
Laboratoire Bois Process, Afocel, Domaine de l'Etançon, Nangis, France.

IP022 -**Giant reed – an alternative raw-material for papermaking**
Sandra Abrantes, Maria Emília Amaral, Ana Paula Costa, and Ana Paula Duarte
Unidade de Investigação de Materiais Têxteis e Papeleiros;
Departamento de Ciência e Tecnologia do Papel, Universidade da Beira Interior, Covilhã, Portugal.

IP023 -**Copolymerisation Kinetics of a Divinyl *p-tert*-Butylcalix[4]arene Derivative and Styrene determined by FT-IR spectroscopy**
Alexandra I. Costa, Patrícia D. Barata, José V. Prata
Secção de Química Orgânica, Departamento de Engenharia Química and Centro de Investigação de Engenharia Química e Biotecnologia, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal.

IP024 = IP056 -**Argilas organofílicas como alternativa para remediação de áreas contaminadas por hidrocarbonetos**
Kleberson R. O. Pereira, Marilda M. G. Ramos Vianna, Meiry G. F. Rodrigues, Francisco R. Valenzuela Diaz
LMPSol, Departamento de Engenharia Metalúrgica e de Materiais, Universidade de São Paulo, São Paulo, SP, Brasil;
LABNOV, Departamento de Engenharia Química, Universidade Federal de Campina Grande, Campina Grande, PB, Brasil.

IP029 -**Surface energy, surface area and SEM imaging of *eucalyptus globulus* fibres network after beating, web forming and sizing**
Graça V.S. Carvalho, José M. R. C. A. Santos, António A. Martins, Margarida L. Figueiredo
Chemical Engineering Department, University of Coimbra, Coimbra, Portugal;
Dept. Chem. Tech., Polytec. Inst. of Bragança, Bragança, Portugal;
RAIZ- Forest and Paper Research Institute, Aveiro, Portugal.

IP030 -**Substituição do carbonato de cálcio pelo gesso na carga mineral de tubos de pvc**
Ivânia S. Lima, Domingos S. H. Malta
Departamento do Básico, Escola Politécnica de Pernambuco, Universidade de Pernambuco, Madalena, Recife, Pernambuco, Brasil;
Departamento de Química, Universidade Católica de Pernambuco, Boa Vista, Recife, Pernambuco, Brasil.

IP031 -**Clonal variation and influence of extractives of *Eucalyptus globulus* Labill. in kraft pulping**
Jorge Gominho, José Rodrigues and Helena Pereira
Centro de Estudos Florestais, Instituto Superior de Agronomia, Lisboa, Portugal;
Forestry and Forest Products Group, IICT, Tapada da Ajuda, Lisboa, Portugal.

IP032 -**Improvement of HZSM-5 zeolite performance in the transformation of bioethanol into olefins by alkaline treatment**
A. Alonso, B. Valle, A. Atutxa, A.G. Gayubo, A.T. Aguayo
Dpto. Ingeniería Química, Universidad del País Vasco, Bilbao.

IP033 -**Biodiesel – Combustível Alternativo**
Pedroso, L.M., Falcão, J., Simões, P.N., Simão, A.V., Portugal, A.
Grupo de Computação, Estatística e Materiais (CEM), Departamento de Engenharia Química, Universidade de Coimbra, Coimbra, Portugal;
Câmara Municipal de Coimbra, Coimbra, Portugal.

IP035 -**Lignin characterization by acetylation procedures**
Carolina Cateto, Filomena Barreiro, Alírio Rodrigues
LSRE - Laboratory of Separation and Reaction Engineering;
Escola Superior de Tecnologia e de Gestão, Instituto Politécnico de Bragança, Bragança;
Faculdade de Engenharia da Universidade do Porto, Porto.

IP036 -**Development of Image Analysis Methods to Evaluate Barley / Malt Grain Size**
António L. Amaral, Orlando Rocha, Cristina Gonçalves, António Augusto and Eugénio C. Ferreira
Universidade do Minho, Departamento de Engenharia Biológica, Braga, Portugal;
Instituto Politécnico de Bragança, Departamento de Tecnologia Química - ESTIG, Bragança, Portugal;
UNICER, Via Norte, Leça do Balio, S. Mamede de Infesta, Portugal.

Lignin Characterization by Acetylation Procedures

Carolina Cateto [1,2], M.N. Belgacem[3], Alírio E. Rodrigues [2], Filomena Barreiro [1,2]

(1) School of Technology and Management, Bragança Polytechnic Institute

(2) Laboratory of Separation and Reaction Engineering, School of Engineering – University of Porto

(3) Ecole Française de Papeterie et des Industries Graphiques, Institut National Polytechnique de Grenoble

Introduction

The amount of the total hydroxyl content of lignin is of great importance in the formulation of a lignin based polyurethane system since it allows the quantity of the polyisocyanate counterpart within the right stoichiometry. In this work, the reliability of an acetylation procedure, regarding the determination of total hydroxyl content of a commercial kraft lignin, was studied.

Some important remarks, concerning lignin acetylation procedures, are given in two fundamental texts edited by Deen and Lin (1992) and Zakis (1994). In practice, the application of acetylation is difficult and subject to the influence of several variables.

Objectives

The objective of this work is to examine the reliability of some typical lignin acetylation procedures. Lignin was acetylated using an acetic anhydride-pyridine mixture and the recovered acetylated samples were analysed by FTIR using KBr pellets. Several experimental conditions were tested:

a) Reaction time and temperature;
b) Composition of the acetylation reagent;
c) Presence or not of a catalyst;
d) Drying process of the acetylated samples.

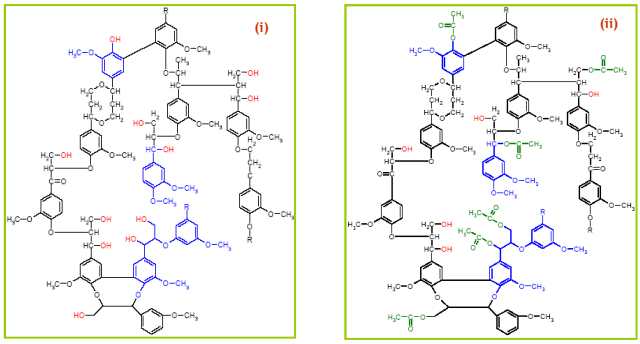

Figure 1. Lignin structural model: (i) original sample and (ii) partially acetylated sample.

Experimental

1. Materials

Lignin was obtained from Meadwestvaco (lignin content of 97% w/w on dry basis). Pyridine, acetic anhydride and imidazole were proanalysis grade (purity over 99.5%). Imidazole was used as received. Pyridine and acetic anhydride were dried over molecular sieves before using.

2. Acetylation procedure

Lignin acetylation was conducted as described in the international standard method ISO 14900:2001 (E). Some modifications were introduced in what concerns the composition of the acetylation reagent and temperature of the reaction. The objective was to cover some of the acetylation conditions published in the available literature and used for different purposes (total hydroxyl determination, GPC and NMR analysis).

Table 1. Resume of the acetylation procedures.

Sample	Lignin (g)	Catalyst (g)	Acetylation Reagent Acetic Acid: Pyridine	Temperature	Reaction Time (min)	Drying
01	1.5010	-	88:12	Heat under reflux	60	At 60 °C until constant weight
02	1.5010	-			120	
03	1.5000	-			180	
04	1.5014	-			15	Freeze drying
05	1.5013	-			30	
06	1.5033	-			45	
07	1.5004	-			60	
08	1.5011	0.7999	88:12		60	
09	1.5002	0.8001	88:12		120	
10	1.5011	0.8001	88:12		180	
11	1.5000	-	80:20		60	
12	1.0009	-	50:50	Room Temperature	24 hours	

3. Lignin recovery procedure

The acetylated lignin was recovered according to the procedure described by Glasser et al. (1993). The recovered lignins were collected and dried: (i) at 60 °C until constant weight and (ii) using freeze drying.

4. FTIR spectroscopy

KBr pellets were prepared with a lignin concentration of 1% (w/w) using a Specac hydraulic press. Fifteen scans per spectrum were taken in the range from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}. A background spectra was systematically collected before the acquisition of the sample spectra.

In order to correct for concentration fluctuations, the spetra were corrected acording to the area of the band assigned at 1507 cm^{-1} (aromatic ring vibration) in the original sample. This vibration was not affected by the acetylation procedure.

Results and Discussion

The major changes observed in the FTIR spectra (original vs acetylated sample) are:

a) Reduction of the hydroxyl (O-H) stretching band centred at 3434 cm^{-1}. This reduction is accompanied by the clear assignment of two bands (3640 and 3520 cm^{-1});
b) Increase in the carbonyl (C=O) stretching region (appearance of two well defined bands at 1737 and 1766 cm^{-1});
c) Increase in carbon-hydrogen bending (C-H) at 1368 cm^{-1};
d) Increase of absorbance in the region assigned between 1010 and 1360 cm^{-1} due to the increase of C-H and C-O deformations in the forming -O-(C=O)-CH_3 group.

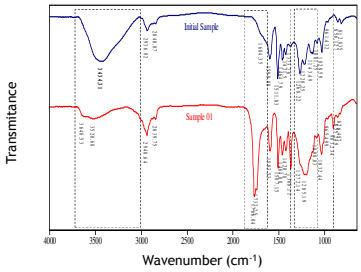

Figure 2. FTIR spectra of a lignin sample: before (initial sample) and after acetylation (sample 01).

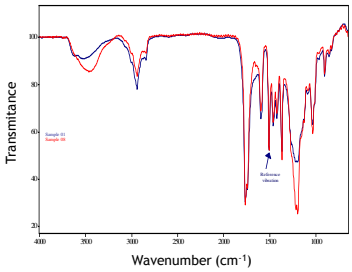

Figure 3. Comparison between two acetylated samples for a reaction time of 1 hour without (sample 01) and with catalyst (sample 08).

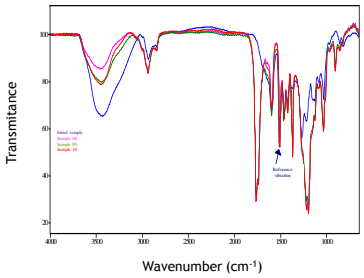

Figure 4. Effect of reaction time (1 to 3 hours) on the acetylation yield of the lignin sample with catalyst.

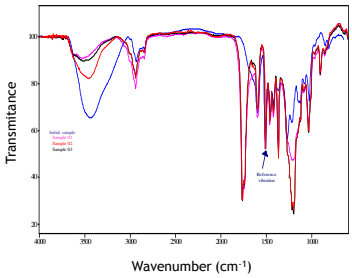

Figure 5. Effect of reaction time (1 to 3 hours) on the acetylation yield of the lignin sample without catalyst.

The obtained results indicated that:

a) The acetylation reaction was incomplete for all the studied conditions. A residual band, assigned to the OH stretching vibration (3410-3460 cm^{-1}), was always observed;
b) Higher reaction times and the presence of catalyst did not increment the reaction yield.
c) The maximum yield of the reaction was obtained for a reaction time of 1 hour (presence or not of a catalyst).

Conclusions

The study presented here point out for incomplete lignin acetylation for all the studied conditions, resulting in an unreliable total hydroxyl determination.

To overcome these difficulties, efforts should be made to optimize the process by careful monitoring. In that way, the experimental procedure presented here could be very helpful.

Acknowledgements: To FCT for financial support (grant SFRH/BD/18415/2004); to MeadWestvaco for supplying us the Indulin AT samples

References: Dence C.W., Lin, S.Y, Ed. Methods in Lignin Chemistry, Springer-Verlag, 1992 ● Zakis, G.F., Funtional analysis of lignins and their derivatives, TAPPI Press, 1994 ● ISO 14900 - Plastics - Polyols for use in the production of polyurethane - Determination of hydroxyl number ● Glasser, Wolfgang G., Davé, Vipul, Frazier, Charles E., Davé, Vipul, Frazier, Charles E., "Molecular Weight distribution of (semi-) commercial lignin derivatives", Journal of Wood Chemistry and Technology, 13(4), 545-559 (1993).